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54 Method for enhancing the biological activity of formulations containing solid imidazoliny benzoic acid esters.

57 There is provided a method for enhancing the biological activity of herbicidal formulations of solid, imidazoliny benzoic acid esters by adjusting the pH of the formulations, when diluted for spray application, to a pH of about 1.0 to 3.8 by the addition of an alkali metal bisulfate, ammonium bisulfate or a mixture thereof.

The invention also relates to a stable, non-aqueous, solid formulations of an imidazoliny benzoic acid ester and an alkali metal bisulfate, ammonium bisulfate or a mixture thereof.

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Imidazoliny benzoic acids, esters and salts are effective for the selective control of a wide variety of undesirable monocotyledonous and dicotyledonous weed species in the presence of cereal crops such as barley, wheat and rye and have been used effectively in this manner in most wheat and barley producing countries around the world. Among the most effective of these compounds is an isomeric mixture of two positional isomers, namely, 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester. In graminaceous crops such as wheat, barley and rye, this isomeric mixture has provided excellent control of many important grasses and broadleaf weeds including wild oats (*Avena* spp.), wind grass (*Apera spicaventi*), black grass (*Alopecurus myosuroides*), wild mustard (*Brassica kaber*), wild buckwheat (*Polygonum convolvulus*), field pennycress (*Thlaspi arvense*) and wild radish (*Raphanus raphanistrum*). However, as the use of the imidazoliny benzoic acid esters has increased and spread to grain producing countries all around the world, it has become increasingly evident that the limited solubility of the above-said esters in aqueous solutions restricts the concentrations of ester obtainable in such solutions and hence their use in aqueous sprays.

As viewed today, organic solvents are recognized as having a potential deleterious effect upon the environment. Moreover, the use of organic solvents in the preparation of pesticide formulations can be hazardous to workers in the formulation and packaging plants and, likewise, to the farmer who is exposed to the formulations during pesticide application if the handling of such formulations is not adequately controlled. Additionally, it is well recognized that use of organic solvents in the preparation of pesticide formulations generally increases the cost of the product, both in manufacture and shipping of the finished formulation.

It would, therefore, be most advantageous if the imidazoliny benzoic acid esters of this invention could be formulated in a manner which would be (1) free of organic solvents, (2) readily dispersed in water for application to the foliage of plants and soil and (3) exhibit enhanced biological activity over an equivalent amount of the ester suspension concentrate formulation applied alone.

The present invention relates to a method for enhancing the biological activity of formulations of aqueous herbicidal dispersions, suspensions, emulsions and the like, in which the herbicidal agent is present as a finely divided, particulate, imidazoliny benzoic acid ester, by adjusting the pH of said aqueous dispersion, suspension, emulsion or the like upon dilution for spraying, to a pH of from 1.0 to 3.8 and preferably to a value between pH 2.0 and pH 3.5, with an alkali metal bisulfate, ammonium bisulfate, or mixture thereof.

More particularly, the invention relates to herbicidal formulations as described above, wherein the herbicidal agent is an isomeric mixture of finely divided, particulate, 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester and the pH of the aqueous composition, when diluted with water for application, is adjusted to a pH value between pH 1.0 and pH 3.8 and preferably between pH 2.0 to 3.5 by addition thereto of from 1.0 to 3.0 molar equivalents of sodium bisulfate, potassium bisulfate, ammonium bisulfate or a mixture thereof per mole of ester present in said aqueous composition.

The invention also relates to stable, non-aqueous, solid formulations comprising from 10% to 55% by weight of a mixture of solid 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid methyl ester; and from 45% to 90% by weight of sodium bisulfate, potassium bisulfate, ammonium bisulfate or a mixtures thereof. Preferred solid formulations are generally comprised of 45% to 55% by weight of the isomeric mixture of the imidazoliny toluic acid methyl esters and about 45% to 55% by weight of the alkali metal bisulfate or ammonium bisulfate.

Because of the limited solubility of imidazoliny benzoic acid esters in water and many other solvents, such esters have been formulated for agricultural application as wettable powders, water dispersible granules, aqueous suspension concentrates and the like. These formulations are generally dispersed in water for application to plants, shrubs, soil or the locus of treatment in the form of an aqueous spray containing the imidazoliny benzoic acid ester as finely divided solid particles. These aqueous sprays are highly effective for the control of a wide variety of weed species but may be of significantly greater value to the farmer if the herbicidal activity of the sprays could be enhanced.

Surprisingly, this invention achieves the above-said desirable biological enhancement of the ester-containing sprays. Moreover, the present invention eliminates use organic solvents in the imidazoliny benzoic acid ester formulations, thus avoiding problems frequently associated with the manufacture, handling or application of solvent-containing formulations. The compositions prepared by the method of the present invention also have the added advantage that they permit the application of lower dosages of the imidazoliny benzoic acid esters while achieving the desired level of weed control and do not contaminate the environment with organic solvents.

Moreover, these advantages are obtained using innocuous alkali metal or ammonium bisulfate rather than strong acids which may be difficult and hazardous to handle at the application site. Importantly, it also appears that the use of alkali metal bisulfate and/or ammonium bisulfate with the formulations containing solid, particulate imidazolinyl benzoic acid ester unexpectedly increases the uptake of the imidazolinyl compound by the plants to which it is applied.

Typical suspension concentrate formulations which may be biologically enhanced, when diluted with water for spray application and pH adjusted in accordance with the present invention, have the following compositions:

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### Suspension Concentrates

15	Compound	% w/v
	Imidazolinyl benzoic acid ester	20.0-30.0
20	Ethoxylated Nonyl phenol with 8-12 Mols of ethoxylation (Nonionic surfactant)	12.0-20.0
25	Oxyethoxylated polyaryl phosphate neutralized with triethanolamine (Dispersing Agent)	1.0-4.0
30	Butyl capped ethylene oxide/propylene oxide block copolymer (Nonionic surfactant)	1.0-3.0
35	Propylene glycol	0.75-3.0
40	Silicone antifoam	0.50-1.0
	Preservative-aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one	0.1-0.2
45	water	100.00

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The tradenames and descriptions of the ingredients employed in the preparation of the above-identified formulations are listed below along with the names of the manufacturers marketing such chemicals.

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	<u>Tradenames</u>	<u>Chemical Descriptions</u>	<u>Manufacturer</u>
5	Arkopal N-080	8 mole nonyl phenol ethoxylate	Hoechst
10	N-110 (Nonionic sur- factant)	11 mole nonyl phenol ethoxylate	Hoechst
15	Soprophor FL (Dispersing Agent)	Oxythoxylated polyarl phosphate neutralized with triethanolamine	Rhone- Poulenc
	Silcolapse 5000	Silicone antifoam	I.C.I. Ltd.
20	Silica FK 320	Precipitated amorphous silica	
	Proxel GXL (Preservative)	Aqueous dipropylene glycol solution of 1,2- Benzisothiazolin-3-one	I.C.I. Ltd.
25	Witconol NS 500K (Dispersing Agent)	Nonionic surfactant: a butyl capped ethylene oxide/propylene oxide block copolymer	WITCO S.A.
30	EMCOL 4061	butyl capped ethylene oxide/propylene oxide block copolymer/propylene glycol ratio = 1/3/1.29 (70% in propylene glycol)	WITCO S.A.
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Typical aqueous flowable formulations that can be enhanced by the method of the present invention are described below:

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Aqueous Flowabl C ncentrates

5	<u>C mpound</u>	<u>% w/v</u>
	Imidazolinyl Benzoic Acid Ester	20 - 40
10	Polyethoxylated nonylphenols ethoxylated with 8-12 Mols of ethoxylation (Nonionic surfactant)	12 - 20
15	Polyethoxylated polyaryylphenol phosphate, neutralized with triethanolamine (dispersing agent)	3 - 5
20	Silicone antifoam agent	0.5 - 1.0
25	Water q.s. to	100.0

30 Polyoxyethylene nonylphenols suitable for use in  
flowable concentrate compositions of the invention

35	<u>Average</u> <u>Ethoxylation</u> <u>(moles)</u>	<u>Kinematic viscosity</u> <u>(25% aqueous solution)</u> <u>centistokes</u>
40	9.5	102
	9.5	87
	10.0	53
45	10.0	43
	10.0	22
	10.5	18
	11.0	30
50	12.0	13

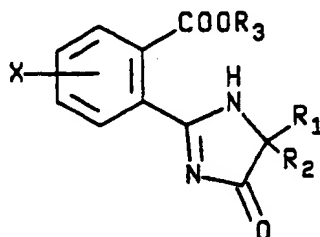
55 To prepare effective flowable concentrates, free of clays and soluble gums and containing 20% to 40% by weight of finely divided, solid, particulate imidazolinyl benzoic acid ester, said ester is dispersed in an aqueous solution containing from 15% to 35% by weight of surfactant which has a kinematic viscosity of about 10 to 100 centistokes at 25% aqueous solution. Surfactants giving kinematic viscosities in the above range permit the use of sufficient quantities of said surfactants to obtain flowable concentrate compositions

containing on a weight to volume basis 20% to 40% of solid, finely ground, imidazoliny benzoic acid ester, 1.0% to 5.0% of wetting/dispersing agents, and 0.5% to 1.0% of antifoam agents, and 0.1 to 0.5% of a preservative and generally having a viscosity of from 1,000 to 3,500 centipoises as measured by a Brookfield viscometer, with a number 2 spindle at 6 rpm at 20°C. These compositions resist settling of the solid components and they do not gel. The kinematic viscosities of these surfactants measured as a 25% aqueous solution, allows the incorporation of high levels of surfactants in the final aqueous flowable compositions, without causing them to become too viscous to process and use easily. The incorporation of high levels of surfactant in the formulation provides the additional benefit that surfactants need not be incorporated during dilution of the flowable composition in a spray tank prior to application, making the compositions of this invention easier and safer to apply.

A typical stable, non-aqueous, composition of the invention comprises about 50% by weight of an isomeric mixture of solid 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester and about 50% by weight of sodium bisulfate.

In accordance with this invention, formulations containing an imidazoliny benzoic acid ester as a finely divided particulate solid when dispersed in water, are herbicidally enhanced by admixture of the diluted aqueous formulation with about 1 to 3 molar equivalents of an alkali metal bisulfate, ammonium bisulfate or a mixtures thereof. Such admixture generally results in adjustment of the pH of the dilute aqueous composition to a value between pH 1.0 to pH 3.8.

Among the imidazoliny benzoic acid esters that are effectively enhanced by the method of the present invention are those represented by the structure:



wherein X is hydrogen, an alkyl C<sub>1</sub>-C<sub>3</sub>, halogen or nitro; R<sub>1</sub> is an alkyl C<sub>1</sub>-C<sub>4</sub>; R<sub>2</sub> is an alkyl C<sub>1</sub>-C<sub>6</sub>, cycloalkyl C<sub>3</sub>-C<sub>6</sub>, or when R<sub>1</sub> and R<sub>2</sub> are taken together with the carbon to which they are attached they may represent a cycloalkyl C<sub>3</sub>-C<sub>6</sub> optionally substituted with methyl; R<sub>3</sub> is an alkyl C<sub>1</sub>-C<sub>12</sub> optionally substituted with one C<sub>1</sub>-C<sub>3</sub> alkoxy group or one C<sub>3</sub>-C<sub>6</sub> cycloalkyl group or one phenyl group, an alkenyl C<sub>3</sub>-C<sub>5</sub> optionally substituted with one or two C<sub>1</sub>-C<sub>3</sub> alkyl group(s) or one phenyl group or with one to two halogen substituent(s), an alkynyl C<sub>3</sub>-C<sub>5</sub> optionally substituted with one or two C<sub>1</sub>-C<sub>3</sub> alkyl group(s) or one phenyl group or with one to two halogen substituent(s), benzyl, cyclohexenylmethyl, ethynylcyclohexyl, ethynylallyl or pentadienyl, cycloalkyl C<sub>3</sub>-C<sub>6</sub> optionally substituted with one or two C<sub>1</sub>-C<sub>3</sub> alkyl group(s); when R<sub>1</sub> and R<sub>2</sub> are not the same, the optical isomers thereof, and the isomeric mixtures thereof.

Other imidazoliny benzoic acid esters that are herbicidally enhanced by the method of this invention are:

- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, 2-propynyl ester;
- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, n-propyl ester;
- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, 1,1-dimethylallyl ester;
- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, allyl ester;
- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, octyl ester;
- (+)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, ethyl ester;
- (+)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, 2-chloroallyl ester;
- (-)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, -2-propynyl ester; and
- 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)benzoic acid, 1-methyl-2-butenyl ester.

The present invention is further illustrated by the examples set forth below.

## 55 EXAMPLES 1-2

### Preparation of Suspension Concentrate Formulations Containing an Imidazoliny Benzoic Acid Ester

To a suitable vessel fitted with a propeller mixer and high shear agitation add 500 L of water. Turn on the mixer and add 7.5 kg of silicone antifoam agent, 1.5 kg of aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one preservative and 42.9 kg of a mixture of butyl capped ethylene oxide/propylene oxide block copolymer and propylene glycol having a 1 to 3 to 1.29 ratio and 10 kg of oxythoxylated polyaryl phosphate neutralized with triethanolamine dispersing agent.

Stirring is continued to dissolve and/or disperse all the additives. Thereafter, the high-shear agitator is switched on and 250 kg of an isomeric mixture of an imidazoliny benzoic acid ester is added. High-shear mixing is continued until a fluid, mobile slurry is achieved with retentions of less than 0.25% on 150 $\mu$  sieve. Avoid air entrainment during mixing. The thus formed slurry is then wet, milled to give a product with a particle size distribution of 90% less than 8 $\mu$  and 50% less than 3 $\mu$ . Thereafter the remaining water added. To this mixture 200 kg of 11 mole nonyl phenol ethoxylate is gradually introduced and stirring is continued to obtain a smooth, uniform aqueous suspension concentrate.

Compositions prepared by this method are reported in Table I below.

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Tabl I

5	Compound	% w/v	
		Ex. 1	Ex. 2
10	6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)- <u>m</u> -Toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)- <u>p</u> -Toluic acid, methyl ester	30.0	25.0
15	Ethoxylated nonyl phenol 11 mols of ethoxylation	15.0	20.0
20	Oxyethoxylated polyaryl phosphate neutralized with Triethanolamine	1.0	1.0
25	Propylene glycol	1.3	1.3
30	Butyl capped ethylene oxide/propylene oxide block copolymer	3.0	3.0
35	Aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one (preservative)	0.15	0.15
40	Silicone antifoam	0.75	0.75
45	Water q.s. to	100.0	100.0

**EXAMPLES 3-14****50 Preparation of stable aqueous flowable concentrates**

The preparation of stable aqueous flowable concentrates that can be biologically enhanced by the method of the present invention when they are tank mixed in the field for dilute aqueous spray application, are generally prepared by a two step procedure as described below.

55 The first step involves the preparation of a ground, particulate, aqueous slurry which requires the calculation of the quantities of each ingredient required and mixing as follows: To a suitable vessel with fitted agitation, add all the water, then the antifoam agent if desired, followed by the wetting and/or dispersing agents and then the isomeric mixture of 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic



acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester. Gradually add this isomeric mixture with vigorous high-shear agitation until a mobile slurry results. Continue high shear-mixing until the particle size is suitable for milling, avoiding air entrainment during mixing.

Then pass the slurry through a wet-mill to give a suspension with particle size essentially 98% less than 5 microns and sample the milled slurry and analyze for active ingredient (% w/w).

The second step involves preparation of the aqueous flowable concentrate.

Calculate the weight of milled slurry required for the final product and add it to a suitable vessel fitted with efficient agitation.

Calculate the extra quantities, if any, of wetting and/or dispersing agents, the antifoam and the antifreeze required in the final product and add them to the slurry. Agitate the mixture until the mixture is homogeneous.

Calculate the quantity of extra water required and add it to the vessel and mix until homogeneous.

Gradually add and dissolve the required amount of surfactant, which as a 25% aqueous solution has a kinematic viscosity of 5 to 100 centistokes, and mix with vigorous agitation, avoiding air entrainment.

Mix thoroughly until all the surfactant is dissolved and a smooth, uniform product is obtained.

Utilizing the above procedure yields the stable aqueous flowable compositions listed in Tables II, III and IV below.

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**Table II**  
**Aqueous Flowable Formulations Containing an Imidazolinyl Benzoic Acid Ester**

Compound	Formulations			
	Ex. 3 % w/v	Ex. 4 % w/v	Ex. 5 % w/v	Ex. 6 % w/v
6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)- $\alpha$ -Toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-Toluic acid, methyl ester	30.0	25.0	30.0	25.0
Arkopal N 110 - Nonionic surfactant- Ethoxylated nonyl ph nol 11 moles EO	12.0	16.0	15.0	20.0
Soprophor FL - Dispersing Agent- oxyethoxylated polyaryl ethoxylate neutralized with triethanolamine	4.0	4.0	4.0	4.0
Silcolapse 5000 - Silicone antifoam	0.75	0.75	0.75	0.75
Proxel GXL - Preservative - aqueous dipropylene glycol solution of 1,2-benzisothiazolin-2-one	0.15	0.15	0.15	0.15
Water, to make	100%	100%	100%	100%
Density	1.04	1.03	1.03	1.03

**Table III**  
**Aqueous Flowable Formulations Containing an Imidazolinyl Benzoic Acid Est I**

Compound	Ex. 8 % w/v	Ex. 9 % w/v
6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)- <u>m</u> -Toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)- <u>p</u> -Toluic acid, methyl ester	25.0	25.0
Arkopal N 100 - Nonionic surfactant - Ethoxylated nonyl Phenol 11 moles EO	15.0	20.0
Dispersing Agent - Soprophor FL/Witconol NB 500K/ Propylene glycol 1/3/1.3	4.0	4.0
Silicone antifoam	0.75	0.75
Preservative - Proxel GXL	0.15	0.15
Water, to make	100.0%	100.0%

**Table IV**  
**Aqueous Flowable Concentrate Containing an Imidazoliny Benzoic Acid Ester**

Isomeric mixture of	Ex. 10 (g/l)	Ex. 11 (g/l)	Ex. 12 (g/l)	Ex. 13 (g/l)	Ex. 14 (g/l)
6-(4-isopropyl-4-methyl-5-oxo-2-imidazolyl-2-yl)-m-tolic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolyl-2-yl)-toluic acid, methyl ester	340.0	283.3	340.0	283.3	226.7
Polyethoxylated nonylphenol (11 Mol EO) viscosity 15 c nterstokes as a 25% aqueous solution (Nonionic surfactant)	120.0	160.0	150.0	200.0	200.0
Wetting/dispersing agent (polyethoxylated polyarylphenol phosphate, neutralized with triethanolamine)	40.0	40.0	40.0	40.0	40.0
Silicone antifoam agent	7.5	7.5	7.5	7.5	7.5
Water (Balance)	532.5	539.2	499.2	499.2	555.8
Stability:					
Storage time	Example No.	Average percent recovery			
One Month	8-12	28 C	37 C	50 C	
Two Months	10-12	100.0	98.0	97.0	
		99.0	98.0	98.0	

Table V  
Suspension Concentrate Formulations for Wild Oat Control Greenhouse  
Test Equivalent to Spray Volume of 100 L/ha

Treatment	Equivalent of g/ha ai	l/ha Formulation	g/ha Sodium Bisulfate	ml/ha 50% 11 mole nonyl phenol ethoxylate
Example I	600	2.00	--	--
Example I	500	1.66	--	--
Example I	400	1.33	--	--
Example I	200	0.67	--	--
Example I	500	1.66	--	100
Example I	400	1.33	--	80
Example I	200	0.67	--	40
Example I	500	1.66	316	100
Example I	400	1.33	253	--
Example I	200	0.67	126	--
Example I	500	1.66	316	100
Example I	400	1.33	253	80
Example I	200	0.67	126	40

300SC = 30% w/v of an isomeric mixture of  
 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and  
 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester

In these biological evaluations test samples are prepared using the 300 SC (suspension concentrate) from Example 1. The test procedure is designed to provide and evaluate the equivalent of 200, 400, 500 or 600 grams per hectare of an isomeric mixture of 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester, applied to wild oats (*Avena fatua*) in the 2 to 3 leaf stage. Formulations evaluated include 300 SC in water alone, 300 SC plus sodium bisulfate in water, 300 SC plus Nonionic surfactant (11 mole nonyl phenol ethoxylate) in water and 300 SC plus sodium bisulfate and nonionic surfactant (11 mole nonyl phenol ethoxylate) in water.

The test compositions are made up in water and sprayed on wild oat plants in the 2 to 3 leaf stage of development and the sprayed plants are then placed on greenhouse benches where they are cared for using normal greenhouse practices. The sprayer is designed and calibrated to deliver the equivalent of 100 litres per hectare of test solution.

Each composition is replicated four times and on days 10 and 20 after spraying, all plants are examined and the percent wild oat control determined for each treatment and recorded. The compositions evaluated and the results obtained are reported in Tables V and VI respectively.

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Table VI

% Wild Oat Control with Example I, 300SC formulation alone or in combination with sodium bisulfate, additional 11 mole nonyl phenol ethoxylate or both sodium bisulfate and additional 11 mole nonyl phenol ethoxylate

Treatment	% Oat Control				Average %
	1	2	3	4	
Example I 300SC 600	75	85	80	85	81.3
Example I 300SC 500	80	80	75	80	78.8
Example I 300SC 400	50	75	75	80	70.0
Example I 300SC 200	50	55	50	60	53.8
Example I 300SC 500	90	90	90	85	88.8
Example I 300SC 400	85	90	85	85	86.3
Example I 300SC 200	80	80	75	80	78.8
Example I 300SC 500	98	98	90	95	95.3
Example I 300SC 400	95	95	95	85	92.5
Example I 300SC 200	50	75	75	65	66.3
Example I 300SC 500	95	95	95	90	93.8
Example I 300SC 400	95	95	90	80	90.0
Example I 300SC 200	50	75	85	80	71.3

AR = 11 mole nonyl phenol ethoxylate

From the above data it can be seen that the addition of sodium bisulfate to the dilute aqueous 300SC formulations of Example 1 increases the control of wild oats from 11.5% to 22.5% over the dilute aqueous 300SC formulations alone. The data also show that the addition of nonionic surfactant to the diluted suspension concentrate helps to increase the biological activity thereof. Moreover, the addition of sodium sulfate and added nonionic surfactant to the suspension concentrate containing imidazolynyl benzoic acid

ester also enhances the biological activity over that obtained with the nonionic surfactant.

#### **EXAMPLE 16**

##### **5 Chemical and Physical Stability of a 1:1 w/w blend of Solid ImidazolinyI Benzoic Acid Ester**

In this evaluation technical grade samples 98% purity of a mixture of 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester are uniformly blended on a 50/50 % w/w basis with sodium bisulfate 96% purity and then  
10 stored in glass jars at room temperature and 37°C. After four months of storage the chemical and physical characteristics of the blends show no evidence of change.

#### **EXAMPLE 17**

##### **15 Determination of the effect of alkali metal bisulfate on ImidazolinyI benzoic acid ester solubility in different types of water using 0, 1, 2 or 3 molar equivalents of alkali metal bisulfate**

In these evaluations the 300SC concentrates of Example I, containing Isomeric mixtures of 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid methyl ester and 2-(4-Isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester are dispersed in water and treated with from 0 to 3 molar  
20 equivalents of sodium bisulfate based on the amount of ester used. The pH of the water was determined before admixture with the 300SC, after admixture with the 300SC and again after treatment with sodium bisulfate.

Also, each sample is assayed for the presence of the isomeric mixture of the esters and likewise for the  
25 isomeric mixture of the corresponding acids to determine where the esters are undergoing any significant hydrolysis.

The results of these evaluations are reported in Tables VII and VIII below.

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Table VII

Determination of the effect of from 1 to 3 molar equivalents of alkali metal bisulfate on aqueous dispersions of Example I, 300SC in different type water samples

Treatment	Water	Canada		Canada		NJ	
		A	B	C	D		
water pH		8.64	8.64	8.59	7.40		
Water + 300SC pH		8.24 milky appearance	8.14 milky appearance	8.14 milky appearance	6.86 milky appearance		
+ 1 molar Equiv. NaHSO <sub>4</sub>		5.14 No apparent change	5.90 No apparent change	3.82 No apparent change	2.73 turned Hazy		
+ 2 molar Equiv. NaHSO <sub>4</sub>		2.75 Slightly Hazy	2.97 No apparent change	2.61 Essentially Clear	2.15 Essentially Clear		
+ 3 molar Equiv. NaHSO <sub>4</sub>		2.12 Essentially Clear	2.32 Essentially Clear	2.10 Essentially Clear	1.67 Essentially Clear		

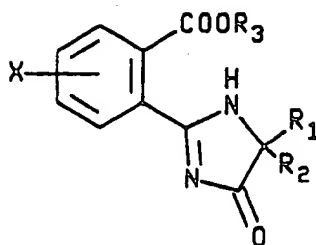
Table VIII

Analytical determinations for the presence of Imidazoliny Benzoic acid ester and corresponding imidazoliny benzoic acid in filtered and unfiltered samples treated with 3008C from Example I and from 1 to 3 molar equivalents of  $\text{NaHSO}_4$

Treatments containing 3008C	% w/w Imidazoliny Benzoic Acid Ester	% w/w Imidazoliny Benzoic Acid
unfiltered Samples		
A	0.422	0.039
B	0.405	0.041
C	0.428	0.014
D	0.454	0.007
filtered Samples		
A	0.187	0.024
B	0.183	0.034
C	0.194	0.031
D	0.214	0.009
filtered Samples + 1 Molar Eq. $\text{NaHSO}_4$		
A	0.204	0.006
B	0.206	0.006
C	0.240	0.007
D	0.457	0.007
filtered Samples + 2 Molar Eq. $\text{NaHSO}_4$		
A	0.436	0.007
B	0.365	0.004
C	0.456	0.006
D	0.450	0.004
filtered Samples + 3 Molar Eq. $\text{NaHSO}_4$		
A	0.464	0.007
B	0.459	0.007
C	0.460	0.004
D	0.461	0.004

## Claims

1. A method for enhancing the biological activity of a formulation containing a solid imidazoliny benzoic acid ester characterized by:
  - (a) diluting the ester containing formulation with water; and
  - (b) adjusting the pH of the diluted ester containing formulation to a value of about 1.0 to 3.8.
2. The method according to claim 1, characterized by the imidazoliny benzoic acid ester having the structure:



wherein X is hydrogen, an alkyl C<sub>1</sub> to C<sub>3</sub>, halogen or nitro; R<sub>1</sub> is an alkyl C<sub>1</sub> to C<sub>4</sub>; R<sub>2</sub> is an alkyl C<sub>1</sub> to C<sub>6</sub>, a cycloalkyl C<sub>3</sub> to C<sub>6</sub>, or when R<sub>1</sub> and R<sub>2</sub> are taken together with the carbon to which they are attached they may represent a cycloalkyl C<sub>3</sub> to C<sub>6</sub> optionally substituted with methyl; R<sub>3</sub> is an alkyl C<sub>1</sub> to C<sub>12</sub> optionally substituted with one C<sub>1</sub> to C<sub>3</sub> alkoxy group or one C<sub>3</sub> to C<sub>6</sub> cycloalkyl group or one phenyl group, an alkenyl C<sub>3</sub> to C<sub>5</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s) or on phenyl group or with one to two halogen substituent(s), an alkynyl C<sub>3</sub> to C<sub>5</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s) or one phenyl group or with one to two halogen substituent(s), benzyl, cyclohexenylmethyl, ethynylcyclohexyl, ethynylallyl or pentadienyl, a cycloalkyl C<sub>3</sub> to C<sub>6</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s); when R<sub>1</sub> and R<sub>2</sub> are not the same the optical isomers thereof, and the isomeric mixtures thereof.

3. The method according to claim 1, wherein the imidazolinyl benzoic acid ester is characterized by an isomeric mixture of solid 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester.

4. The method according to claim 1 wherein the pH is adjusted with a bisulfate.

5. The method according to claim 4, wherein the bisulfate is selected from the group consisting of an alkali metal bisulfate, an ammonium bisulfate or a mixture thereof.

6. The method according to claim 5 wherein the alkali metal bisulfate is selected from the group consisting of sodium bisulfate and potassium bisulfate.

7. A method for enhancing the biological activity of an herbicidal formulation containing a solid imidazolinyl benzoic acid ester characterized by:

(a) diluting the ester containing formulation; and

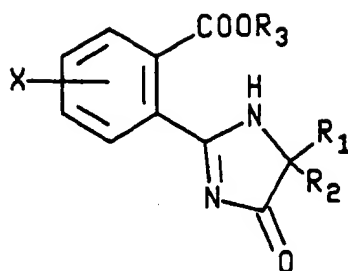
(b) adjusting the PH of the ester containing formulation to a value of about 1.0 to 3.8 by the addition of an alkali metal bisulfate, an ammonium bisulfate or a mixture thereof.

8. The method according to claim 7, wherein the imidazolinyl benzoic acid ester is characterized by an isomeric mixture of solid 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester.

9. The method according to claim 7, wherein the alkali metal bisulfate is selected from the group consisting of sodium bisulfate and potassium bisulfate.

10. A composition characterized by a solid imidazolinyl benzoic acid ester produced by the method in claim 7.

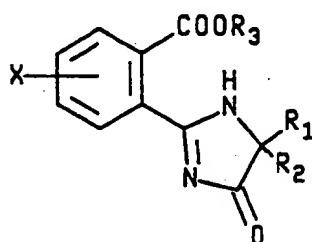
11. A method for increasing the biological activity of an herbicidal formulation characterized by a solid imidazolinyl benzoic acid ester having the structure:



wherein X is hydrogen, an alkyl C<sub>1</sub> to C<sub>3</sub>, halogen or nitro; R<sub>1</sub> is an alkyl C<sub>1</sub> to C<sub>4</sub>; R<sub>2</sub> is an alkyl C<sub>1</sub> to C<sub>6</sub>, a cycloalkyl C<sub>3</sub> to C<sub>6</sub>, or when R<sub>1</sub> and R<sub>2</sub> are taken together with the carbon to which they are attached they may represent a cycloalkyl C<sub>3</sub> to C<sub>6</sub> optionally substituted with methyl; R<sub>3</sub> is an alkyl C<sub>1</sub> to C<sub>12</sub> optionally substituted with one C<sub>1</sub> to C<sub>3</sub> alkoxy group or one C<sub>3</sub> to C<sub>6</sub> cycloalkyl group or one phenyl group, an alkenyl C<sub>3</sub> to C<sub>5</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s) or one phenyl group or with one to two halogen substituent(s), an alkynyl C<sub>3</sub> to C<sub>5</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s) or one phenyl group or with one to two halogen substituent(s), benzyl, cyclohexenylmethyl, ethynylcyclohexyl, ethynylallyl or pentadienyl, a cycloalkyl C<sub>3</sub> to C<sub>6</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s); when R<sub>1</sub> and R<sub>2</sub> are not the same the optical isomers thereof, and the isomeric mixtures thereof, by admixing with the diluted aqueous composition about 1 to 3 molar equivalents of sodium bisulfate, potassium bisulfate, ammonium bisulfate or a mixture thereof, based upon the amount of imidazolyl benzoic acid ester in the composition.

12. The method according to claim 11 wherein the imidazolyl benzoic acid ester is characterized by an isomeric mixture of 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester; and the bisulfate is sodium bisulfate.

13. A stable, non-aqueous, solid formulation characterized by 10% to 55% by weight of an imidazolyl benzoic acid ester having the structure:



wherein X is hydrogen, an alkyl C<sub>1</sub> to C<sub>3</sub>, halogen or nitro; R<sub>1</sub> is an alkyl C<sub>1</sub> to C<sub>4</sub>; R<sub>2</sub> is an alkyl C<sub>1</sub> to C<sub>6</sub>, a cycloalkyl C<sub>3</sub> to C<sub>6</sub>, or when R<sub>1</sub> and R<sub>2</sub> are taken together with the carbon to which they are attached they may represent a cycloalkyl C<sub>3</sub> to C<sub>6</sub> optionally substituted with methyl; R<sub>3</sub> is an alkyl C<sub>1</sub> to C<sub>12</sub> optionally substituted with one C<sub>1</sub> to C<sub>3</sub> alkoxy group or one C<sub>3</sub> to C<sub>6</sub> cycloalkyl group or one phenyl group, an alkenyl C<sub>3</sub> to C<sub>5</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s) or one phenyl group or with one to two halogen substituent(s), an alkynyl C<sub>3</sub> to C<sub>5</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s) or one phenyl group or with one to two halogen substituent(s), benzyl, cyclohexenylmethyl, ethynylcyclohexyl, ethynylallyl or pentadienyl, a cycloalkyl C<sub>3</sub> to C<sub>6</sub> optionally substituted with one or two C<sub>1</sub> to C<sub>3</sub> alkyl group(s); when R<sub>1</sub> and R<sub>2</sub> are not the same the optical isomers thereof, and the isomeric mixtures thereof, and from 45% to 90% by weight of sodium bisulfate, potassium bisulfate, ammonium bisulfate or a mixture thereof.

14. The formulation according to claim 13 characterized by 45% to 55% by weight of an isomeric mixture of 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester and 45% to 55% by weight of sodium



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## EUROPEAN SEARCH REPORT

Application Number

EP 91 10 3162

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 256 414 (AMERICAN CYANAMID CO.) ---		A 01 N 43/50 // (A 01 N 43/50 A 01 N 59:02 )
A	FR-A-2 321 845 (RICHTER GEDEON VEGYESZETI GYAR RT.) ---		
A	FR-A-2 247 976 (E.I. DU PONT DE NEMOURS AND CO.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 01 N
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		24 July 91	DONOVAN T.M.
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